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THERMAL PROPERTIES OF METHYL-METHACRYLATE-N-VINYLCARBAZOLE COPOLYMERS

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ABSTRACT

Copolymers of methyl methacrylate /MM/-N-vinylcarbazole /NVC/ were synthesized and their thermal properties were studied. The effect of NVC content on thermal behaviour of copolymers was investigated. Based on TG,DTG analysis ,the kinetic parameters of thermal degradation processes were computed.

INTRODUCTION

Considering the widely known low thermal stability of polymers a lot of attemps are made to produce the polymers of improved thermal properties.Out of the number of different ways for synthesis such polymers we took into consideration the copolymerization reaction. The monomers used were : MM and NVC.The effect of NVC content in copolymers on their thermal properties was examined.It was expected that such copolymers should have higher thermal stability than PMM, due to the outstanding thermal stability of PNVC./1-3/.

Kinetic parameters of the thermal degradation processes were computed basing on the numerical method of kinetic parameters estimation of the given kinetic equation /4/.

MEASURING METHODS

MM-NVC copolymers were obtained by suspension copolymerization /5/. Thermal studies were carried out using a Thermoanalyzer TA-2 /Mettler, Switzerland/. The measurements were carried out in an inert/argon/ and oxidizing /air/ atmosphere at a heating rate of 3^{o}/min and with a sample weight of o.050g.

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RESULTS AND DISCUSSION

There were carried out two series of TG,DTG and DTA measurements for MM-NVC copolymers containig ca 5 - 48% NVC in an inert and oxidizing atmosphere in temperature range 25 -500°C. Based on the obtained thermograms the temperatures of the begining ofweight loss and the changes of weight loss, in the above temperature range were determined and shown in Fig.1. In the air as well in argon atmosphere, the values of weight loss differed considerably dependantly on the copolymer composition. The maximum value of weight loss and the minimum temperature of the begining of the decomposition process /T_o/ was observed for PMM. The increase of NVC content in copolymers caused the rise of $T_o$values, while the weight loss remarkably decreased. The data calculated for some copolymers are listed below:

Sample /%NVC/	atmosphere T_o/°C/ air	argon	weight loss at 350°C/%/ air	argon
PMM	263	237	84.1	81.8
16.9	279	250	38.2	28.7
47.9	300	290	8.8	5.9

Moreover, the analysis of DTG curves indicated that the temperature of the maximum decomposition rate was shifted towards the higher temperature range when the content of NVC in copolymers was increased, eg. for : PMM -326°C/air/,323°C/argon/,16,9%NVC -354°C, 368°C, 47.9%NVC - 383°C, 396°C, respectively.

On DTG curves other less intensive peaks were also observed, which revealed the complexity of the given thermal degradation process. The thermal effects taking place during samples heating,registered on DTA curves are shown in FIG. 2. In case of PMM the endothermal processes of melting, depolymerization and evaporation occured at 290 -350°C.For the copolymers the endothermal changes appeared in higher temperature range. The temperature rise was related to the introduced amount of NVC - the more NVC in copolymer, the higher temperature range. These results confirmed thermally stabilizing influence of NVC monomer units on copolymer stability.

In case of some copolymers the exothermal changes were also noticed. Probably these changes were the result of the mutual inter-

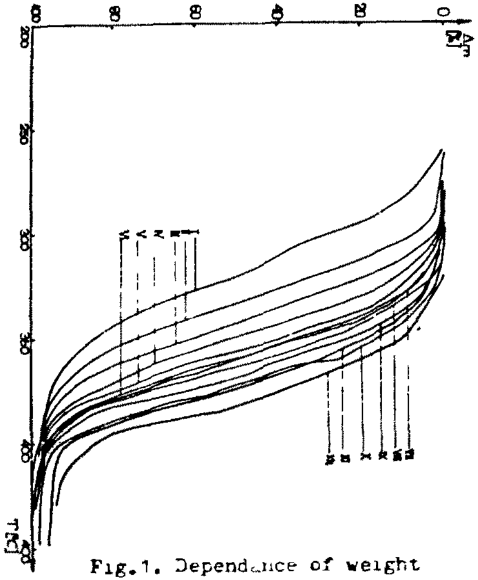

Fig.1. Dependance of weight loss for MA-NVC copolymers.Contents of NVC-see Fig.2. atmosphere: air

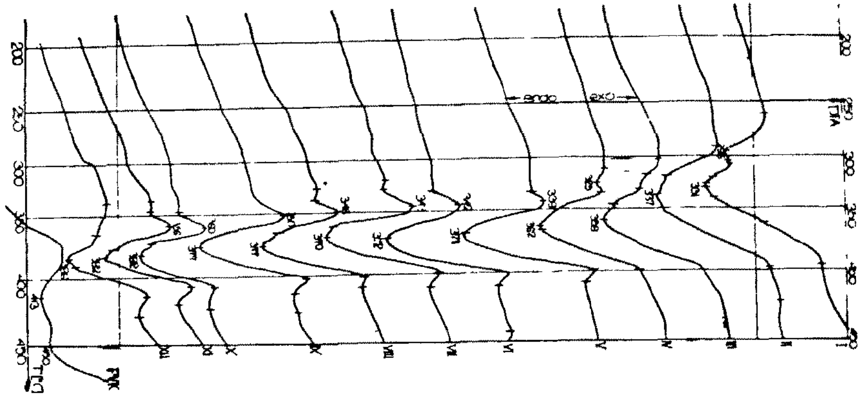

Fig.2.DTA curves of MA-NVC copolymers ./atmosphere: air/.
Contents of NVC in copolymers:
I - MA, II - 4,9 ,III - 8.9%,IV - 12.9%,V - 16.9%,
VI- 20.9% ,VII - 25.4%,VIII - 28.8 ,IX - 33.9%,
X - 37.0%,XI - 41.0%,XII - 47.9%.

action between NVC and MM monomer units, leading to the formation of cyclic systems and probable processes of branching and crosslinking of copolymer chains. At the present stage of work, the mechanism of these reaction is not evaluated.

The computed values of kinetic parameters i.e. activation energy /E_a/ ,reaction rate coefficient /A/ and reaction order /n/,are compiled in Table 1 for some copolymers.

Table 1. The kinetie parameters of some MM-NVC copolymers./argon/

NVC ctn. in copol. /%/	E_a /kcal/mol°K/	A	n
16.9	34.65	24.06	0.78
25.4	33.04	25.08	0.53
37.0	37.03	26.75	0.71
47.9	38.21	28.28	0.47
47.9^x air	39.14	38.48	0.29

E_a and A values for the studied copolymers were approximately of order 33 - 40 kcal/mole°K, however for the copolymers containing the greater amount of NVC these values became higher.

CONCLUSIONS

The obtained copolymers MM-NVC exibited the improved thermal stability in comparison to PMM. It was stated that with an increase of NVC content in copolymers a considerable decrease of weight loss was observed and at the same time the values of temperature of maximum decomposition rate as well as the range of thermal changes were shifted towards higher temperature region.

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